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Biomimetic Photo-Actuation: Progress and Challenges

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ABSTRACT

Photo-actuation, such as that observed in the reversible sun-tracking movements of heliotropic plants, is produced by a complex, yet elegant series of processes. In the heliotropic leaf movements of the Cornish Mallow, photo-actuation involves the generation, transport and manipulation of chemical signals from a distributed network of sensors in the leaf veins to a specialized osmosis driven actuation region in the leaf stem. It is theorized that such an arrangement is both efficient in terms of materials use and operational energy conversion, as well as being highly robust. We concern ourselves with understanding and mimicking these light driven, chemically controlled actuating systems with the aim of generating intelligent structures which share the properties of efficiency and robustness that are so important to survival in Nature. In this work we present recent progress in mimicking these photo-actuating systems through remote light exposure of a meta-stable state photoacid and the resulting signal and energy transfer through solution to a pH-responsive hydrogel actuator. Reversible actuation strains of 20% were achieved from this arrangement, with modelling then employed to reveal the critical influence hydrogel pK_a has on this result. Although the strong actuation achieved highlights the progress that has been made in replicating the principles of biomimetic photo-actuation, challenges such as photoacid degradation were also revealed. It is anticipated that current work can directly lead to the development of high-performance and low-cost solar-trackers for increased photovoltaic energy capture and to the creation of new types of intelligent structures employing chemical control systems.

Keywords: hydrogel, actuator, light, soft robotics, biomimetic, plants, chemical, distributed sensors

1. INTRODUCTION

Intelligent structures – devices or systems that respond autonomously to changes in their environment – mimic the adaptively of plants and animals. By using smart material actuators – materials which directly respond to environmental stimuli – in these devices, the structural, sensing and movement functions can be performed by a *single* component, as opposed to a conventional intelligent structure where these functions are performed by *different* components, linked with complicated electronics and mechanisms. As a result, intelligent structures that employ smart material actuators more closely mimic both the resilience as well as the material and structural efficiency found in Nature. Although it may seem that the simplified solution offered by smart material actuators is preferable, such an approach struggles to accommodate complexities such as the physical separation of sensing and actuating locations, multiple or distributed sensors, or the ability to apply computation, control regimes or simple filtering between the sensing and actuating functions. In this work we explore biomimetic photo-actuation with a case study of a sun-tracking plant, the Cornish Mallow (*Lavatera cretica* L.), to reveal how Nature creates efficient and robust intelligent structures, while still allowing for the complexities required for rich adaptivity¹.

In Nature, it is the abundance of solar energy that has seen the evolution of light sensitivity in plants, and resulting photosynthesis become one of the most important processes on Earth. In engineering, it is the high degree of spatial and temporal control offered by light as a stimulus which has encouraged the development of many different types of synthetic photo-responsive compounds, such as spiropyrans² and azobenzenes³, as well as photo-responsive smart material actuators, including some types of liquid crystal elastomers^{4,5} and gels⁶. These smart material actuators, although consisting of many different compositions, all respond with changes in geometry (strain state) upon direct exposure to the light stimulus. While

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this co-location of sensing and actuation within the single material is a common property of smart material actuators, it is not common to Nature's intelligent structures. As shown in Video 1, the Cornish Mallow (*Lavatera cretica* L.) reversibly moves its leaves throughout the day such that they remain facing the moving sun. This property, termed heliotropism, involves the generation, transport and manipulation of chemical signals from a distributed network of sensors in the leaf veins to a specialized osmosis driven actuation region in the leaf stem¹. It is this spatial separation of the location of stimulus recognition (light sensing) and response (actuation), which can allow biomimetic systems that share the operating principles of the Cornish Mallow to overcome the constraints of smart material actuators. For example, signals can be integrated (computed) from a range of sensors, filtered and control logic, analogous to a closed-loop proportional-integral-derivative (PID) scheme, applied before being transmitted to the actuator. The Cornish Mallow achieves this while retaining its 'solid-state' type structure, devoid of discrete hinges or separated components, maintaining the benefits of efficient material use with the reduced mechanical complexity that makes smart material actuators so attractive.



Video 1. The reversible sun tracking leaf movements of the Cornish Mallow through a summer afternoon. The leaves moves from left to right (South to West) before returning right to left as the sun sets. This motion back to its starting position is also observed as the leaves are obscured by shadows. <https://youtu.be/idxwLae3Mf0> and <http://dx.doi.org/doi.number.goes.here>

To this end, we are developing a biomimetic analogue of the Cornish Mallow. To achieve this we are employing a meta-stable state photoacid (long lived yet reversible fall in pH upon light exposure) as the sensing and signal transmission element and a pH-responsive hydrogel as an actuating element. Techawanitchai *et al.* used a similar combination of components to create a light sensitive smart material actuator, although a non-reversible photoacid generator was employed, significantly limiting the material's cycle life^{7,8}. Shi *et al.* attempted to overcome this limitation by actuating a pH-responsive hydrogel with a meta-stable state photoacid they developed, but were unable to achieve reversibility from the hydrogel used⁹. Both of these works only employed direct light exposure of the hydrogel material, thus displaying neither signal nor energy transfer through solution and eliminating the potential for control functionalities to be applied. It is anticipated that a biomimetic analogue of the Cornish Mallow could find direct application as a low-cost solar-tracker for increased photovoltaic energy capture. This work also serves to evaluate how the principles of distributed and separated light driven chemical control of actuators can be applied in other types of engineering systems.

In this report a review is undertaken of the key functionalities of the Cornish Mallow before outlining an approach to replicating these functions in an engineered system. Results are then presented of experiments that demonstrate the sensing, signal transfer and actuation elements of the system. The experiments involved the remote light exposure of a meta-stable photoacid and the resulting signal and energy transfer through a gently stirred solution to a pH-responsive hydrogel actuator, shielded from direct light exposure. Results serve to highlight both the progress that has been made in creating truly biomimetic photo-actuation systems, but also the great challenges that exist in developing structures with the intelligence of the Cornish Mallow.

2. THE CORNISH MALLOW

The sun-tracking movements of the Cornish Mallow were investigated by Schwartz and Koller *et al.*¹⁰⁻¹⁶ and Fisher *et al.*¹⁷⁻¹⁹ in the 1980s. Despite this, the full complexity of its operation remains to be elucidated, although we can report with some certainty around key features regarding the perception of light (sensing), signal generation and transport, as well as the control and actuation.

2.1 Sensing

Blue light (410-500 nm) is detected in the Cornish Mallow by photoreceptor molecules in the major leaf veins^{12,15} (Figure 1(a)). Although the exact nature of the responsible molecule(s) that are involved in the Cornish Mallow's light perception are unknown, blue light photoreception in other plants has been attributed to the plasma membrane flavoproteins, phototropin and cryptochrome²⁰.

Schwartz and Koller hypothesized that the photoreceptor molecules have a fixed orientation with respect to the leaf vein (Figure 1(b)) after performing experiments where leaves were illuminated at 45° (oblique light) with different combinations of veins shielded (Figure 1(c))¹⁵. This hypothesis was further supported by later work that showed the plants preferential response when illuminated with light at 45°-55° from above and the influence of light polarization¹².

The experiments performed and configuration hypothesized by Koller *et al.* shows how the Cornish Mallow's response to light is a function of the stimulus of a distributed network of sensors, providing both a means for generating a control signal that is proportional to the error in orientation, while also providing a protecting level of redundancy.

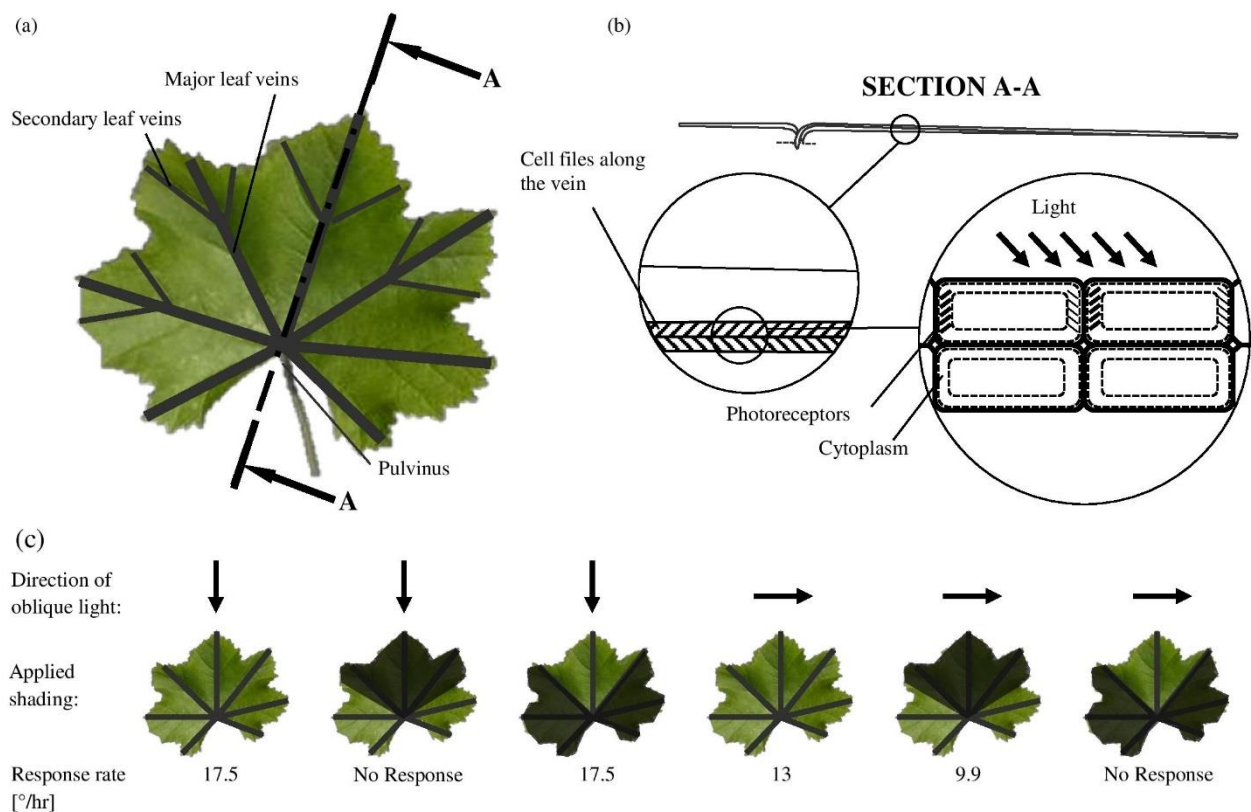


Figure 1. (a) The leaf of the Cornish Mallow. (b) Hypothesized arrangement/orientation of photoreceptors within the leaf veins¹⁵, and (c) the experiment that encouraged this conclusion. Adapted from Dicker *et al.*¹.

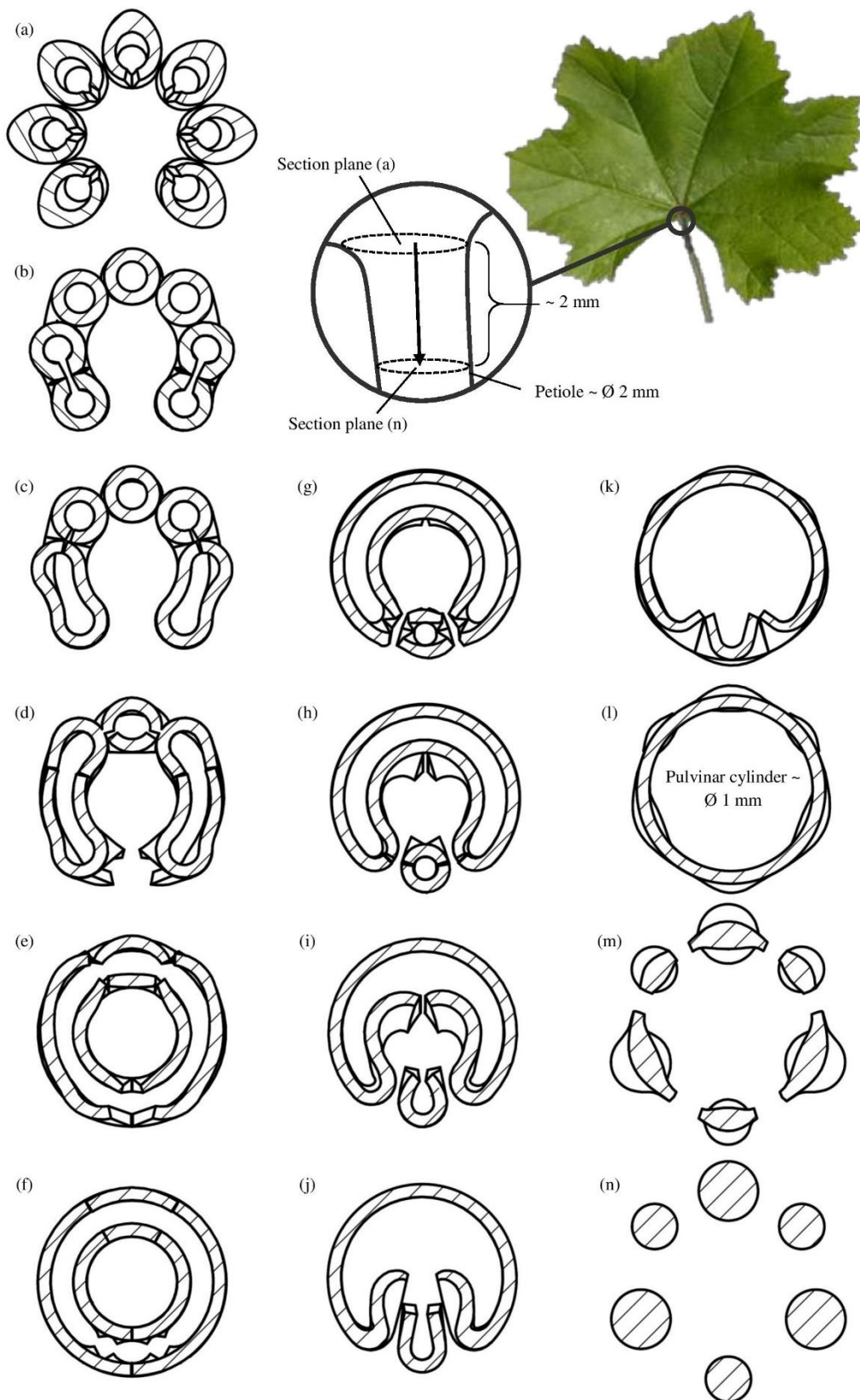


Figure 2. Rearrangement of the vascular phloem and xylem cell files in the Cornish Mallow¹⁸. Adapted from Dicker *et al.*¹.

2.2 Signaling and Control

The signaling of plant movement in various species is known to involve a range of chemicals (hormones or turgorins) including auxin (indole-3-acetic acid), gibberellin, ethylene, abscisic and jasmonic acid as well as sulfonated gallic acid glucoside²¹. The exact processes involved in the sun tracking of the Cornish Mallow are unknown. The chemical signals, whatever their form, are transported from the sensor elements through the vascular xylem and phloem tissues of the leaf veins.

By employing a chemical signal, as opposed to an electronic signal as found in engineered devices, the signal response relationship may be highly complex, with influence from both the current signal state and non-linear rate dependency. This can be thought of as being somewhat analogous to the integrative and derivative function in an engineering PID controller. Furthermore, one could hypothesize that the diffusive nature of chemical signals facilitates signal smoothing (noise filtering) and allows for straightforward signal integration. Thus, the signaling of the Cornish Mallow may in itself be an important part of providing the function of control.

However, control is most obviously imparted to the sun tracking of Cornish Mallow through the geometry of the vascular network that carries the chemical signals. Fisher *et al.* showed that the cell files of phloem and xylem undergo an extremely complicated rearrangement and combination as they move from the intersection of the leaf and stem, to the actuating pulvinus region (Figure 1(a)), located just a millimeter or so beneath this point¹⁸. This vascular rearrangement is shown in Figure 2.

This rearrangement provides computation, integrating the signals of different strengths from the distributed sensors network (the veins), while allowing for elimination of signal conflicts. The rearrangement also serves a structural function, ensuring the stiff vascular tissue is arranged for reduced stiffness in the flexible pulvinus region.

2.3 Actuation

There is a substantial quantity of literature examining biomimetic plant actuation, a pursuit that is expected to yield highly efficient actuation solutions^{22–27}. Actuation in the Cornish Mallow occurs through bending of the pulvinus region of the leaf stem, a process caused by differential cell pressure (turgor), an osmotic process²⁵. Osmosis is the process that sees the movement of solvent (water) from a region of low solute (ion) concentration to a higher one. Studies of pulvinar motor cells in other plants indicate that the signaling hormone auxin activates the proton pump enzyme H^+ -ATPase, creating an electrochemical gradient for the activation of ion transporters for increased uptake of potassium (K^+) and chloride (Cl^-) ions, leading to the osmotic pressurization²⁸. The reverse process is driven by abscisic acid activated chloride efflux channels, and accompanying efflux of cations to maintain charge neutrality²⁸.

Examples of engineered osmosis driven actuators including the work of Su *et al.*²⁹ and Philen *et al.*²³. Osmosis is also the dominant process in the swelling of pH-responsive hydrogel actuators, as employed in our biomimetic analogue of the Cornish Mallow.

3. A BIOMIMETIC ANALOGUE OF THE CORNISH MALLOW

In an attempt to demonstrate the merits of employing the functional strategies of chemical sensing, control and actuation of intelligent structures, as displayed by the Cornish Mallow, it is proposed to create a simplified biomimetic analogue of its sun tracking leaf (Figure 3). The device has just two sensing “veins” and actuators, such that its movement is restricted to that of bending in a single plane.

3.1 Sensing, Signaling and Control

The device will employ the protonated merocyanine meta-stable state photoacid of Shi *et al.*⁹. This water soluble component responds to visible light illumination (419 nm and 570 nm specifically) to change from a weak to a strong acid. Upon removal of light, the compound returns to its original state in around 5 minutes at ambient temperature. It is the transfer and interactions/kinetics of the liberated protons from the strong acidic form of the reacted photoacid that lead to both the signal and energy transfer as well as aspects of system control.

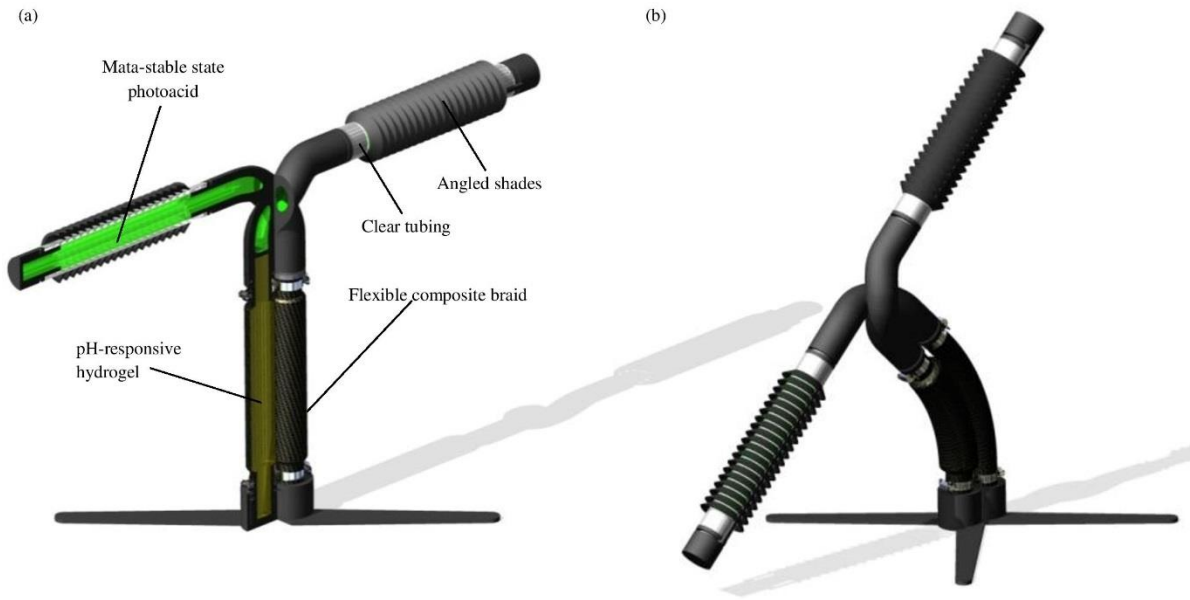


Figure 3. (a) Simplified biomimetic analogue of the Cornish Mallow in its unactuated state with quarter section removed to reveal internal components. (b) Device in its actuated configuration with sensor “veins” normal to light source. Adapted from Dicker *et al.*¹.

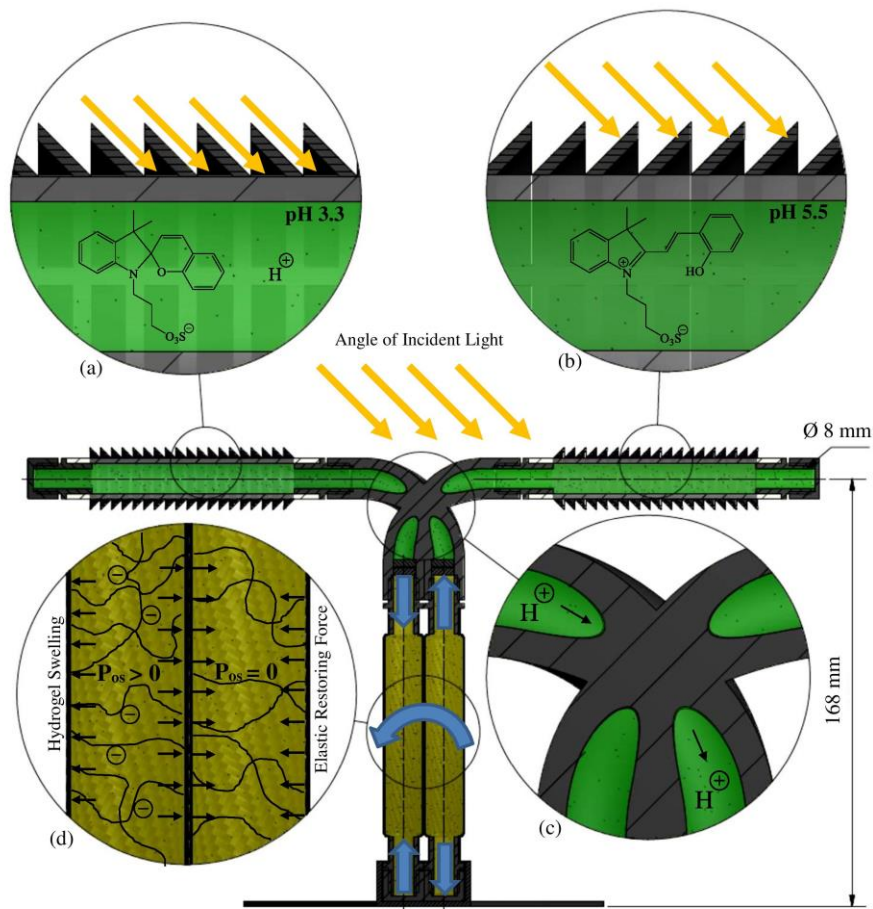


Figure 4. Half section depiction of device (a) and (b) showing proposed shading generated proportion light sensing, (c) acidic signal transmission and (d) actuation. Adapted from Dicker *et al.*¹.

Elaborating on the system control aspects, the amount and rate of pH change created by this photoacid should be a function of the current state of the solution, allowing for signal generation akin to the integrative function in a PID controller (the signal is dependent on the past error state of the system). Furthermore, it is believed that there is a non-linear relationship between the rate of pH change and the current system state, thus we have a rate dependent element, which again is in an abstract way analogous to the derivative element of a PID controller. While the diffusive nature of pH concentration changes leads to signal smoothing, which could be considered as a means for noise cancelling (signal filtering). The geometry of the device, specifically the diffusion distance from the sensors to the actuator, and actuator internal structure will also have significant influence on the resulting actuating signal.

It is likely that the most important aspect of the control system is the design of the sensor veins which expose the photoacid to the light stimulus. One way to replicate the hypothesized photo receptor orientation with respect to the veins of the Cornish Mallow in the biomimetic equivalent is to cover clear tubes, which contain the photoacid, with angled shades. As shown in Figure 4(a) and (b), this aims to set the level of exposure, and thus the pH of the photoacid at a value proportional to the error in light alignment. This effect is analogous to the proportional component of a PID controller.

3.2 Actuation

The scheme proposes the use a pH-responsive hydrogel as the actuator elements. These soft, wet polymers composed of acidic or basic components are able to swell to many times their original size upon changes in the pH (log of proton concentration) of their environment, in the range of the polymers pK_a (log of its proton association/dissociation constant). The accompanying proton association/dissociation leads to a fixed charge being established in the polymer, the resulting influence of this charge sees a differential being established in solute ionic concentration between the inside and outside of the hydrogel. It is this osmotic pressure which drives water in or out of the hydrogel, and creates the swelling.

pH-responsive hydrogels efficiently convert chemical energy into mechanical work with large free strains and moderate blocking forces. However, the slow diffusion driven rate of hydrogel swelling, mechanical fragility and inherent difficulties of turning the three-dimensional swelling of these materials into a targeted actuation whilst maintaining fluid supply makes applying macroscale hydrogels in real devices a significant challenge. To meet these challenges we are investigating the use of hydrogel swelling as a pressure source within a braided flexible composite. This provides practical containment for the hydrogel whilst converting the swelling into a targeted axial contraction with improved work capacity³⁰. Meanwhile, work is ongoing into employing carefully engineered microporous structures to improve the speed of response³¹, and to develop semi-interpenetrating polymer network (semi-IPN) hydrogels for improved toughness with minimal impact on actuator performance. These hydrogels are based on the polyacrylic acid/polyurethane (PAA/PU) semi-IPN hydrogels of Naficy *et al.*³². Critically, as explored through modelling in Section 4.2, the hydrogel pK_a must lie in the range of the pK_a change of the meta-stable state photoacid from its base ($pK_a = 7.75$) to excited states ($pK_a = 4.3$) for actuation to occur³³. Although the pK_a of PAA derived hydrogels should lie in this region, the effective pK_a of hydrogels is a continuing area of investigation.

4. PROGRESS AND CHALLENGES

4.1 Materials and Methods

A meta-stable state photoacid is synthesized as per literature⁹, from which three batches of saturated solutions with deionized water were formed ($\sim 2 \times 10^{-4}$ M) over the course of testing. All experiments were conducted within 8 hours of the solution being made.

Semi-IPN PAA/PU hydrogels were prepared with a modified formulation as found in³². Porous hydrogels of this formulation were prepared by using sodium chloride, as received (Fisher) ~ 220 μ m particles, as a porogen. The hydrogels were UV-cured (365 nm 4W) for 2 hours in 1 mm and 4.5 mm diameter cylindrical molds (for 3 mm and 6.5 mm swollen diameter hydrogels, respectively).

Experimental results were obtained from a custom test apparatus (Figure 5). A rectangular magnetically stirred glass reaction vessel is partially sealed and fed with nitrogen to limit absorbed atmospheric contaminants. This vessel is surrounded on three sides by mirror shielding, which incorporates three 10W 405 - 410 nm LED's (Ledengin LZ4-40UA00-00U8) and three 10W 520 - 535 nm LED's (Ledengin LZ4-40G108-0000), fan cooled and driven at 700 mA. On the fourth side of the reaction vessel is a sample holder connected to a sealed rigid external frame. The sample holder is

backed with mirror shielding to prevent direct light exposure of the hydrogel and photoacid solution in the immediate vicinity of the sample, as shown in Figure 5(b). The sample holder aligns the hydrogel for imaging (Canon 450D, EF 100mm f/2.8 USM Macro lens) with this imaging arrangement providing negligible geometric distortion. Image lighting is provided by a LED ring light with orange light filter. Lighting without the filter was found to lead to unwanted photoacid activation. The pH and temperature are both monitored in the reaction vessel (Mettler Toledo, S20 SevenEasy, InLab Expert probe).

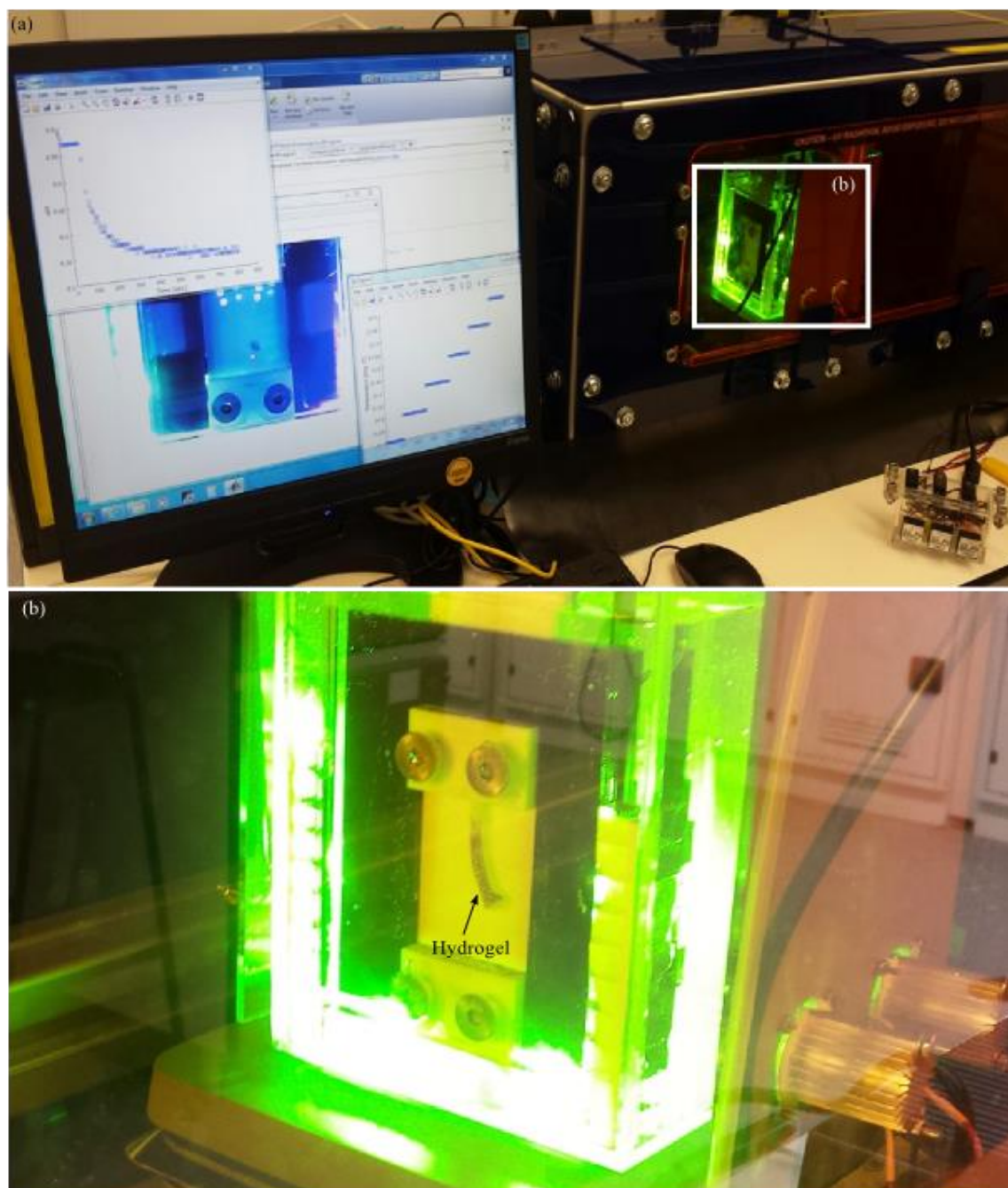


Figure 5. Custom test apparatus. (a) The reaction vessel is illuminated green as viewed through the orange tinted protective shielding, while the sample as shown on the monitor captures the blue light. The plots on the monitor are pH and Temperature. Images are post processed to determine hydrogel displacements. (b) Detail image of 3 mm Ø cylindrical hydrogel shielded from direct light exposure.

The modeling undertaken involves solving numerically the system component equilibrium and mass balance equations, as reported previously by Dicker *et al.*³⁴ but with updated meta-stable state photoacid equilibrium constants from Vallet *et al.*³³.

4.2 Results

The pH change offered by the different batches of photoacid upon illumination was found to be between 1.5 and 1.7 units, with the starting (dark or base state) pH in the range of 5.55 to 5.95. The pH drop was found to be fully recovered after ~5 minutes in the dark. Although ambient room lighting did not initiate the pH drop, close proximity to a low intensity white light source, or placing the solution in a sunny window would see the reaction occur. This sunlight driven activation is critical for the biomimetic devices envisaged, and is shown in Video 2, with the pH change indicated by the photochromic reaction (color change) from a red/orange to a yellow/green.



Video 2. Sunlight driven activation of 1 L of meta-stable state photoacid solution, as shown by the photochromic transition from red/orange (left, high pH) to yellow/green color (right, low pH). https://youtu.be/m_WfybTrEB8 and <http://dx.doi.org/doi.number.goes.here>

The low light intensity required for the photo-reaction to occur and the long stable state of this reaction are both desirable properties. However, these properties mean that the range of high intensity lighting levels provided by the custom lighting rig is unable to create a significant difference in the observed systems equilibrium pH condition (Figure 6). Even the lowest level of lighting produced by the test apparatus sees the photo-reaction proceed to completion so much faster than the reverse reaction that almost no proportional control influence can be observed in the system. This is shown in Figure 6, where we see the pH-time relationship for photoacid illumination under one, two and all three sets of lights in the test apparatus. Although further testing under lower lighting intensities is required, the results shown in Figure 6 suggest that achieving a distributed range of pH conditions (proportional influence) through simple shading may be difficult and that forced solution flow may be required to limit the duration of light exposure in the sensor veins of the biomimetic analogue.

Although the pH change offered is modest and recovery time short when compared to both the pH change and duration usually employed for hydrogel actuation, it does span the expected pK_a for PAA derived hydrogels. This condition suggests potential for actuation even from this modest pH shift, provided the concentration of deprotonated (basic) groups of the PAA hydrogel is not so high as to buffer the photoacid provided drop in pH. In addition, the diffusion distances in the hydrogel must be small enough for hydrogel actuation to occur in a reasonable period of illumination. As a result, the testing employed a small porous hydrogel (3 mm diameter in swollen state) in combination with 1 L of gently stirred photoacid. The resulting actuation of this small cylindrical hydrogel under 15 minutes of illumination with one set of lights and 35 minutes of recovery is shown in Video 3. To the authors' knowledge, this is the first reported example of reversible

spatially separated photo-mechanical energy transduction through a chemical solution intermediary. No obvious degradation in performance was observed after three cycles, and reduction of the photoacid solution down to a volume of 0.65 L also showed no change in actuation performance. This last point, combined with the range of the observed pH drop by the addition of the hydrogel, suggests buffering is not significant issue for the small amount of hydrogel used.

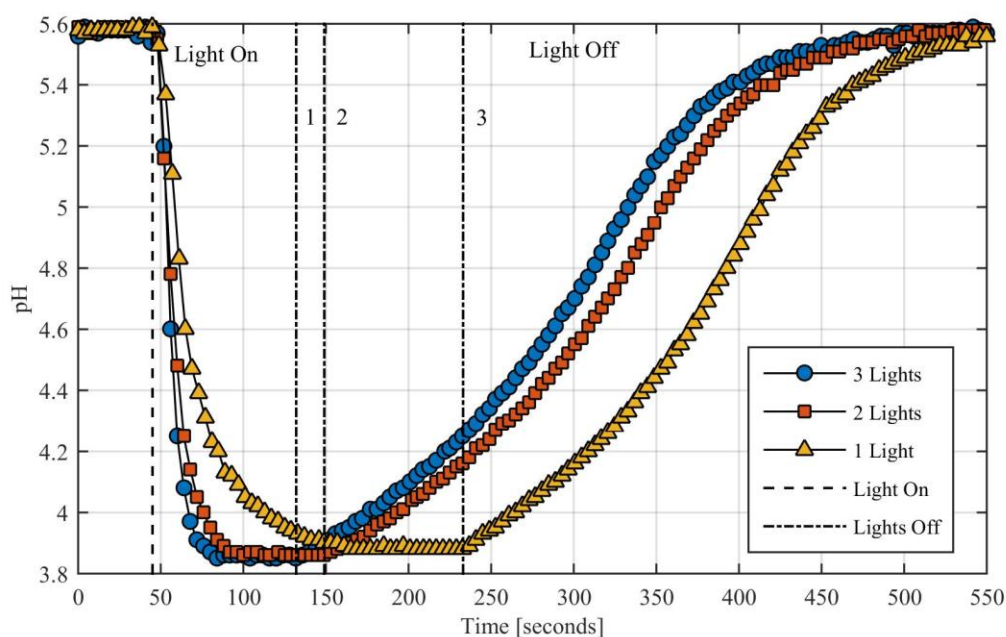


Figure 6. pH-time relationship for illumination of 1 L of gently stirred meta-stable state photoacid for different levels of light intensity. Test performed at 27°C.



Video 3. Light driven reversible hydrogel actuation. Image shows the actuated sample over a faded representation of the hydrogel in the unactuated state <https://youtu.be/9w2Rrggup68> and <http://dx.doi.org/doi.number.goes.here>

Figure 7 shows the measured actuation strain from both the small hydrogel shown in Video 3, and a larger 6.5 mm diameter hydrogel. It can be seen that both hydrogels do not appear to have reached an equilibrium state in actuation strain after 15

minutes illumination, despite this being significantly longer than the time required for the reverse photoacid reaction to occur. Since the hydrogel is shielded from direct light exposure (assuming that any photoacid in the hydrogel is not being activated to its low pH state), this result suggests that there is a significant preferential diffusion of water/hydronium ions over the photoacid into the hydrogel, thus the dimensions of the hydrogel actuator are not firmly restricted to being such that full actuation can occur quickly within the time for the photoacid to revert back to its dark high pH state.

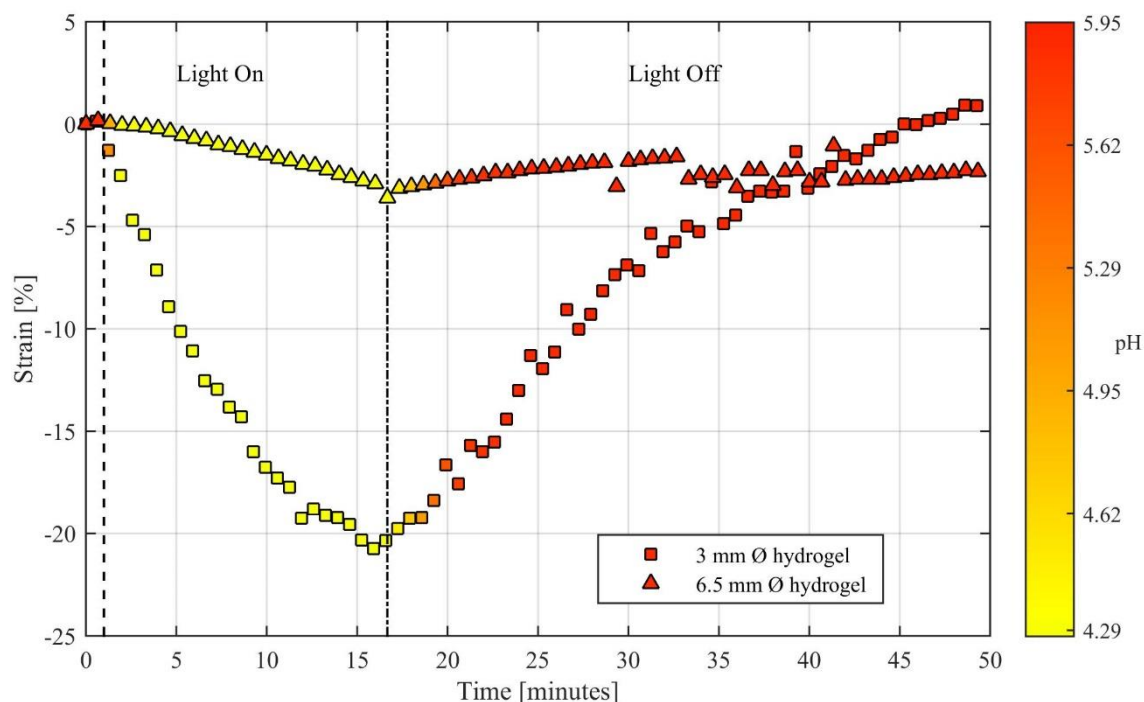


Figure 7. Hydrogel strain, calculated as change in hydrogel length divided by original length and expressed as a percentage is calculated from images. With the length being measured as the distance between 10 points along the length of the hydrogel to account for sample bending. The solution pH at each data point is indicated by the color of the data point, from the high pH red/orange to the low pH yellow/green. It can be seen that the full solution pH change occurs very quickly in comparison to the actuation of the hydrogel.

Although the 20% strain observed in this work is good in comparison to many smart material actuators, it is only a fraction of the actuation potential of the hydrogel used herein. In fact, actuation of this hydrogel from equilibrium in 0.1 M buffer solutions at pH 11 to equilibrium at pH 3 yields a strain of over 200%. Even accounting for the lack of convergence in strain observed in the photoacid tests, it is clear that the photoacid illumination is not able to fully activate the hydrogel. The experimental results showed that measurable buffering of the pH drop had been avoided, this is in part because of the use of a small volume of hydrogel relative to photoacid, but it may also indicate that the range of the pH change offered and its location on the pH scale (where the hydrogel pK_a is relative to the pH drop) is not optimal. This is examined through basic modelling methods and highlighted in Figure 8. The exact pK_a of the hydrogel is unknown, with work on similar semi-IPN PU/PAA hydrogels finding it to be as high as 6.9, while for most PAA based hydrogels it is considered close to 4.3, the value for the acrylic acid monomer³⁴. Furthermore, it is expected that this value is affected by such factors as the ionic strength of the solution, and also for there to be an element of hysteresis to this value. However, the model results, combined with both the limited influence measured by a reduction in photoacid solution volume (1 L to 0.65 L) and the low strain potential achieved in the experiments suggests the hydrogel pK_a is not optimal for this photoacid system. In any event, as shown in Figure 8, even ideal alignment of the hydrogel pK_a to the pH change offered yields just under 60% hydrogel activation under modelled experimental conditions. As a result, full activation of the hydrogel will require a larger shift in the photoacid pK_a from the dark to illuminated states (a larger pH change). Regardless of this finding, a ~20% strain should be sufficient for the creation of a biomimetic photo-actuating device.

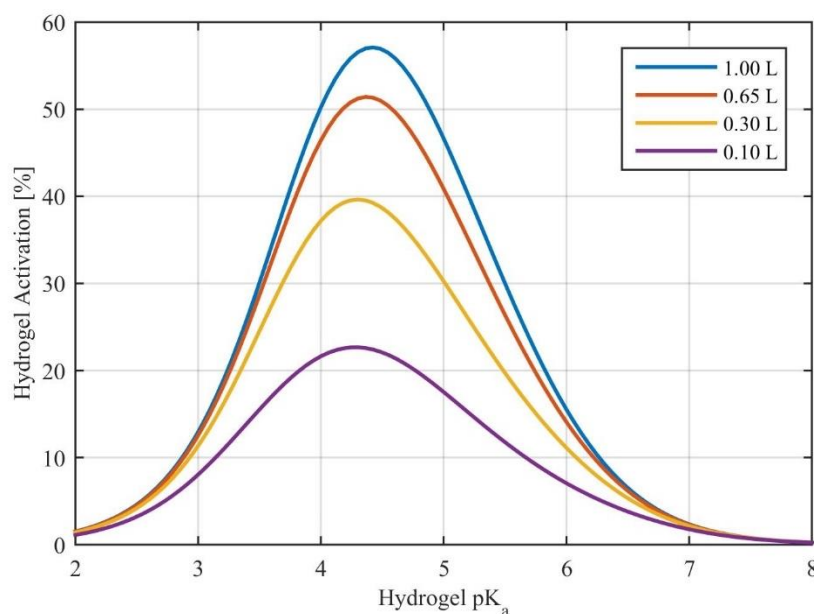


Figure 8. Model of hydrogel activation with 2×10^{-4} M photoacid solutions of different volumes. Hydrogel activation calculated as the change in COOH deprotonation as a percentage of total COOH concentration between the two photoacid states. Model hydrogel closely matches the experimental 3 mm diameter sample with a dry hydrogel volume of 2.7×10^{-8} m³ and a COOH concentration in hydrogel of 0.29 M.

Despite the progress demonstrated from the successful actuation of the hydrogel, there is one significant challenge that has been revealed in the course of this work. Almost complete degradation of the photoacid solution to a non-responsive compound with lower pH was observed over the course of several days, with the process occurring faster at slightly elevated temperature (Figure 9). Discussions with the developer of the photoacid has revealed that changing the composition of the solvent away from pure water to organic solvents or solvent mixtures limits this degradation³⁵. Although switching solvents may have a positive effect on the photoacid stability, the effect on the hydrogel actuation performance is less clear, with any change likely resulting in significant changes in the proton activity and thus pH/swelling relationship. Furthermore, careful selection of solvents will be required to prevent material degradation of the hydrogel.

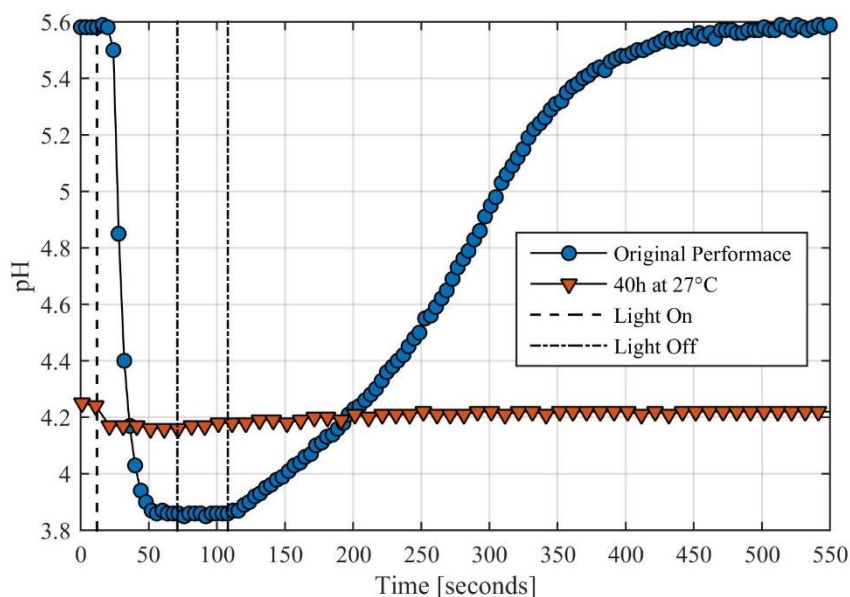


Figure 9. Degradation of photoacid solution, with it loosing almost all of its photoactive pH shift after 40 hours at 27°C.

5. CONCLUSION

This work has contended that the creation of engineered intelligent structures that mimic the sensing, signal transition, control and actuation strategies of Nature's intelligent structure, such as the sun-tracking Cornish Mallow plant, could result in creations that are both efficient and robust, without compromising the system complexities required for rich adaptivity. These include distributed sensors and the spatial separation of those sensing elements to those responsible for actuation and the application of filtering and control schemes to the signals passed between these elements.

The first experiments in attempting to replicate this complexity, through the actuation of a pH-responsive hydrogel by the remote illumination of a meta-stable state photoacid have been shown. In doing so we have demonstrated the first reported example of reversible spatially separated photo-mechanical energy transduction through a chemical solution intermediary. Although the results are promising, with 20% reversible strain being observed, the response of the system was found to degrade over several days. Future work examining the use of different solvent systems will be required to address this limitation.

It is anticipated that the work presented will aid greatly in the development of a biomimetic analogue of the sun tracking Cornish Mallow. While further research may lead to the application of light triggered, chemically controlled hydrogel actuators is a range of intelligent structures and systems.

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REFERENCES

- [1] Dicker, M. P. M., Rossiter, J. M., Bond, I. P., Weaver, P. M., "Biomimetic photo-actuation: sensing, control and actuation in sun-tracking plants," *Bioinspir. Biomim.* **9**(3), 036015, IOP Publishing (2014).
- [2] Hirshberg, Y., "Reversible Formation and Eradication of Colors by Irradiation at Low Temperatures. A Photochemical Memory Model," *J. Am. Chem. Soc.* **78**(10), 2304–2312, American Chemical Society (1956).
- [3] Zimmerman, G., Chow, L.-Y., Paik, U.-J., "The Photochemical Isomerization of Azobenzene 1," *J. Am. Chem. Soc.* **80**(14), 3528–3531, American Chemical Society (1958).
- [4] Finkelmann, H., Nishikawa, E., Pereira, G. G., Warner, M., "A New Opto-Mechanical Effect in Solids," *Phys. Rev. Lett.* **87**(1), 015501 (2001).
- [5] Camacho-Lopez, M., Finkelmann, H., Palfy-Muhoray, P., Shelley, M., "Fast liquid-crystal elastomer swims into the dark," *Nat. Mater.* **3**(5), 307–310 (2004).
- [6] Tomatsu, I., Peng, K., Kros, A., "Photoresponsive hydrogels for biomedical applications," *Adv. Drug Deliv. Rev.* **63**(14-15), 1257–1266, Elsevier B.V. (2011).
- [7] Techawanitchai, P., Ebara, M., Idota, N., Aoyagi, T., "Light-induced spatial control of pH-jump reaction at smart gel interface," *Colloids Surf. B. Biointerfaces* **99**, 53–59, Elsevier B.V. (2012).
- [8] Techawanitchai, P., Ebara, M., Idota, N., Asoh, T.-A., Kikuchi, A., Aoyagi, T., "Photo-switchable control of pH-responsive actuators via pH jump reaction," *Soft Matter* **8**(10), 2844 (2012).
- [9] Shi, Z., Peng, P., Strohecker, D., Liao, Y., "Long-lived photoacid based upon a photochromic reaction," *J. Am. Chem. Soc.* **133**(37), 14699–14703 (2011).
- [10] Werker, E., Koller, D., "Structural specialization of the site of response to vectorial photo-excitation in the solar-tracking leaf of *Lavatera cretica*," *Am. J. Bot.* **74**(9), 1339–1349 (1987).
- [11] Schwartz, A., Koller, D., "Diurnal phototropism in solar tracking Leaves of *Lavatera cretica*," *Plant Physiol.* **80**(18), 778–781 (1986).
- [12] Koller, D., Ritter, S., Briggs, W. R., Schäfer, E., "Action dichroism in perception of vectorial photo-excitation in the solar-tracking leaf of *Lavatera cretica* L," *Planta* **181**(2), 184–190 (1990).

- [13] Koller, D., "Light-driven leaf movements," *Plant, Cell Environ.* **13**(7), 615–632 (1990).
- [14] Koller, D., Levitan, I., "Diurnal phototropism in leaves of *Lavatera cretica* L. under conditions of simulated solar-tracking," *J. Exp. Bot.* **40**(9), 1059–1064 (1989).
- [15] Schwartz, A., Koller, D., "Phototropic response to vectorial light in leaves of *Lavatera cretica* L.," *Plant Physiol.* **61**, 924–928 (1978).
- [16] Koller, D., Zamski, E., "The Phototropic Pulvinus of Bean *Phaseolus vulgaris* L. - Functional Features," *Plant Biol.* **4**, 584–594 (2002).
- [17] Fisher, F. J. F., Wright, M., "The dependence of suntracking in *Lavatera cretica* L. upon carbon dioxide availability," *New Phytol.* **98**(2), 241–248 (1984).
- [18] Fisher, F. J. F., Ehret, D. L., Hollingdale, J., "The pattern of vascular deployment near the pulvinus of the solar-tracking leaf of *Lavatera cretica* (Malvaceae)," *Botany* **65**(10), 2109–2117 (1987).
- [19] Fisher, F. J. F., Fisher, P. M., "Differential starch deposition: a 'memory' hypothesis for nocturnal leaf movements in the sun-tracking species *Lavatera cretica* L.," *New Phytol.* **94**(4), 531–536 (1983).
- [20] Hohm, T., Preuten, T., Fankhauser, C., "Phototropism: translating light into directional growth," *Am. J. Bot.* **100**(1), 47–59 (2013).
- [21] Moran, N., "Osmoregulation of leaf motor cells," *FEBS Lett.* **581**(12), 2337–2347 (2007).
- [22] Skotheim, J. M., Mahadevan, L., "Physical limits and design principles for plant and fungal movements," *Science* **308**(5726), 1308–1310 (2005).
- [23] Philen, M. K., Shan, Y., Prakash, P., Wang, K. W., Rahn, C. D., Zydney, A. L., Bakis, C. E., "Fibrillar network adaptive structure with Ion-transport actuation," *J. Intell. Mater. Syst. Struct.* **18**, 323–334 (2006).
- [24] Burgert, I., Fratzl, P., "Actuation systems in plants as prototypes for bioinspired devices," *Philos. Trans. A. Math. Phys. Eng. Sci.* **367**(1893), 1541–1557 (2009).
- [25] Martone, P. T., Boller, M., Burgert, I., Dumais, J., Edwards, J., Mach, K., Rowe, N., Rueggeberg, M., Seidel, R., et al., "Mechanics without muscle: biomechanical inspiration from the plant world," *Integr. Comp. Biol.* **50**(5), 888–907 (2010).
- [26] Wereley, N. M., Sater, J. M., eds., *Plants and Mechanical Motion A Synthetic Approach to Nastic Materials and Structures*, DEStech Publication inc., Lancaster, Pennsylvania (2012).
- [27] Sinibaldi, E., Puleo, G. L., Mattioli, F., Mattoli, V., Di Michele, F., Beccai, L., Tramacere, F., Mancuso, S., Mazzolai, B., "Osmotic actuation modelling for innovative biorobotic solutions inspired by the plant kingdom," *Bioinspir. Biomim.* **8**(2), 025002 (2013).
- [28] Iino, M., "Auxin- and abscisic acid-dependent osmoregulation in protoplasts of *phaseolus vulgaris* pulvini," *Plant Cell Physiol.* **42**(11), 1219–1227 (2001).
- [29] Su, Y. C., Lin, L., Pisano, A. P., "A water-powered osmotic microactuator," *J. Microelectromechanical Syst.* **11**(6), 736–742 (2002).
- [30] Dicker, M. P. M., Weaver, P. M., Rossiter, J. M., Bond, I. P., "Hydrogel core flexible matrix composite (H-FMC) actuators: theory and preliminary modelling," *Smart Mater. Struct.* **23**(9), 095021 (2014).
- [31] Dicker, M. P., Weaver, P. M., Bond, I. P., Rossiter, J. M., Faul, C. F., "Hydrogel core flexible matrix composite (H-FMC) actuators," 20th Int. Conf. Compos. Mater., 2103–2, Copenhagen (2015).
- [32] Naficy, S., Spinks, G. M., Wallace, G. G., "Thin, Tough, pH-Sensitive Hydrogel Films with Rapid Load Recovery," *ACS Appl. Mater. Interfaces* **6**(6), 4109–4114 (2014).
- [33] Vallet, J., Micheau, J.-C., Coudret, C., "Switching a pH indicator by a reversible photoacid: a quantitative analysis of a new two-component photochromic system," *Dye. Pigment.* (2015).
- [34] Dicker, M. P. M., Bond, I. P., Rossiter, J. M., Faul, C. F. J., Weaver, P. M., "Modelling and Analysis of pH Responsive Hydrogels for the Development of Biomimetic Photo-Actuating Structures," *MRS Proc.* **1718**, mrsf14–mrsf1718 – b21–01, Cambridge University Press (2014).
- [35] Liao, Y., personal corresependent (2016).